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Mössbauer Studies on Oxo-neptunates: Comparison between Hexavalent and Tetravalent Neptunium*

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Amongst the actinide elements the most appropriate nuclide for Mössbauer spectroscopy is ^{237}Np [1]. Most of the studied ternary oxides of neptunium are isostructural with the corresponding well measured uranium compounds. Thus arguments related to lattice symmetries are mutually applicable.

The oxo-neptunates $Li_5Np(VII)O_6$, $Li_6Np(VI)O_6$, $BaNp(VI)O_4$, $Np(IV)GeO_4$, $SrNp(IV)O_3$ and $BaNp(IV)O_3$ were studied by Mössbauer methods. The data presented are supplemented by those taken from magnetic, X-ray crystallographic and thermodynamic measurements [2–4].

Experimental and Results

Mössbauer spectra were taken in standard transmission geometry using metallic ^{241}Am as source material. The source was kept in a helium bath while the temperature for the absorber samples could be varied between 3.5 K and 77 K.

The absorber preparations were performed by allowing NpO_2 to react with the relevant metal oxide under specific conditions, as outlined in the literature [5]. The parameters evaluated from the spectra of the investigated Np compounds are listed in Table I, together with information on the crystal structure.

Discussion

In the compounds studied, the oxidation state of the neptunium ions was 6+ and 4+. The two valence states are reflected in the following parameters.

Isomeric Shift δ

For each oxidation state δ takes up values within a characteristic interval [6]. Within these characteristic ranges the δ values are more negative (positive) for ionic (covalent) bonds and depend also on the ion–ion distance. Np(VI) exhibits a stronger negative δ than Np(IV). This is readily understood because each 5f electron reduces the s-electron density at the position of the nucleus due to screening effects. Since for the nuclear mean square radii

$$\langle R_e{}^2\rangle - \langle R_g{}^2\rangle < 0, \delta(\mathrm{Np(IV)}) > \delta(\mathrm{NP(VI)})$$

Quadrupole Splitting eQV_{zz}

The coordination symmetry of the ion within the crystal expresses itself by the electric hyperfine splitting parameter eQV_{zz} and the asymmetry coefficient η. In oxides Np(VI) often appears in the form of $(NpO_2)^{2+}$ neptunyl groups. This generally linear arrangement with characteristically short binding lengths leads to considerable distortions of the electron configuration and consequently high field gradients. No neptunyl group can exist in Np(IV)

TABLE I. Parameters Evaluated from Mössbauer Spectra[a]

	eQV_{zz} (mm s^{-1})	η	δ/$NpAl_2$ (mm s^{-1})	T_c (K)	$g\mu H$(O) (mm s^{-1})	Crystal structure
($Li_5Np(VII)O_6$)	34 ± 1	0.34 ± 0.03	−78 ± 2			hexagonal
$Li_6Np(VI)O_6$	20 ± 1	0.22 ± 0.01	−58 ± 2			hexagonal
$BaNp(VI)O_4$	105.3 ± 0.1	0.37 ± 0.03	−54 ± 2	18.2 ± 0.3	16.0 ± 0.5	orthorhombic
$Np(IV)GeO_4$	−5 ± 1	~0	−8.1 ± 0.1	~4.8	38.1 ± 0.1	tetragonal
$SrNp(IV)O_3$	~0	~0	−5.6 ± 0.2	–	–	cubic
	23.8 ± 0.5[b]	0.37 ± 0.03[b]	−10.2 ± 0.2[b]	30.5 ± 0.5	45.0 ± 0.5	orthorhombic
$BaNp(IV)O_3$	11.0	~0	−11.2	48 ± 1	51.2 ± 0.5	orthorhombic

[a] The values given for eQV_{zz}, η, δ, and $g\mu H$(O) refer to 4.2 K. $Li_5Np(VII)O_6$ is also listed because it is usually formed when $Li_6Np(VI)O_6$ is prepared. Thus the spectra have to be analysed considering both complexes. [b] Values taken at 77 K.

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compounds. In addition, the three 5f electrons of the Np(IV) ion form a configuration closer to spherical symmetry than the one electron in Np(VI). For compounds of tetravalent neptunium all Np–O distances are virtually equal. Thus eQV_{zz} is, in general, close to zero. Lattice distortions, however, lead to finite values, as in the case of $SrNp(IV)O_3$.

Magnetic Properties

Because of the unfilled 5f shells both Np(IV) and Np(VI) compounds should show temperature-dependent magnetism. Magnetic ordering is therefore to be expected. Whether or not it is observed depends, as it turns out, more on the individual structure of the compound, *i.e.* the Np–Np distance, than on the valence state of the ion. This will be illustrated below.

It is elucidating to plot the evaluated Mössbauer parameters *versus* structural data of the compounds studied. The latter are scarce for neptunium oxides, thus data for the isostructural uranium compounds were also used. Such interdependences are given in Figs. 1 to 3, where our own data were supplemented by others given in refs. 1 and 7.

The isomeric shift δ depends on the Np–O distance, as Fig. 1 demonstrates: the longer the N–O bond, the smaller the isomeric shift. A large δ value results from a high s-electron density at the position of the nucleus. This can be realized by keeping the shielding spatially extended. This, indeed, is true for long neptunyl groups.

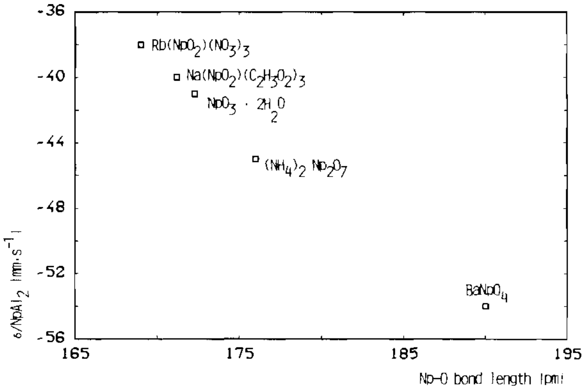

Fig. 1. The dependence of the isomeric shift on the Np–O bond length for hexavalent neptunium.

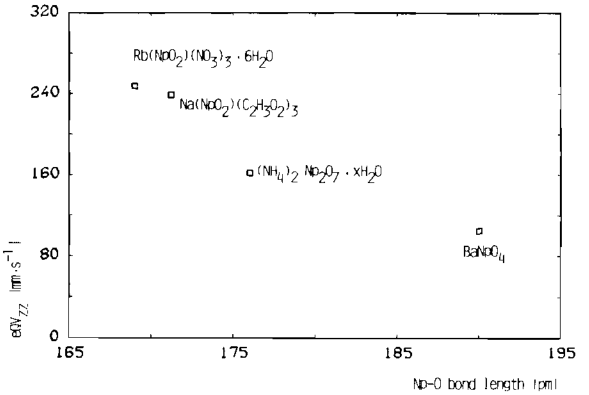

Fig. 2. The dependence of the quadrupole coupling on the Np–O bond length for hexavalent neptunium.

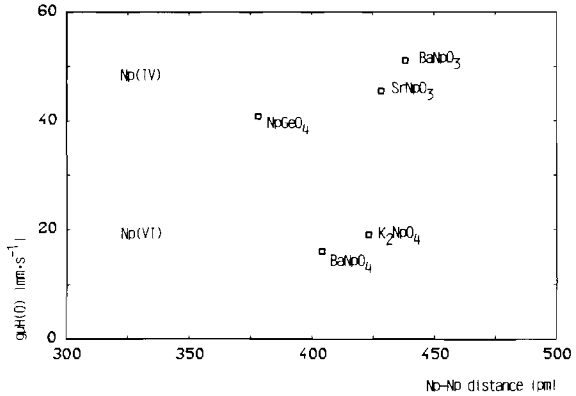

Fig. 3. The magnetic hyperfine term is dependent on the valence state of the neptunium ion and the Np–Np distance within the crystal.

The quadrupole coupling eQV_{zz} similarly depends on the Np–O bond length, as shown in Fig. 2. There is an approximately linear correlation: the longer the Np–O length, the weaker the electric field gradient. The principal axis of V_{zz} points along the neptunyl axis, since the essential field creating charges are two oxygen ions of the $(NpO_2)^{2+}$ group.

The magnetic properties of the compounds studied have been presented and discussed in some detail in refs. 8 and 9. Vital for the appearance of magnetic ordering is the Np–Np distance. The term $g\mu H(0)$ is plotted *versus* this Np–Np separation in Fig. 3. It turns out that the amount of the magnetic hyperfine field is larger for Np(IV) than for Np(VI) compounds. This results from the contribution of orbital electrons which is larger by a factor of about 1.5 for Np(IV) in comparison to Np(VI) ions. The coupling seems to be antiferromagnetic, because for smaller Np–Np distances $g\mu H(0)$ decreases.

Amongst the Np compounds reported in this paper only Li_6NpO_6 does not show any magnetic ordering. $NpGeO_4$ seems to be exceptional, since the Np–O–Np bridges are not stretched but form an angle slightly smaller than 180°.

In Fig. 4 the transition temperatures T_c are plotted *versus* the Np–Np distances for a series of Np oxides. The full symbols refer to Np compounds. A critical distance for the Np–Np magnetic exchange interaction seems to be 460 pm with respect to ordering phenomena [9]. For larger distances the Np–Np exchange interaction is too small (at least for temperatures >4 K), independent of the crystal structure.

The interdependences between crystallographic data and isomeric shift, electric hyperfine splitting

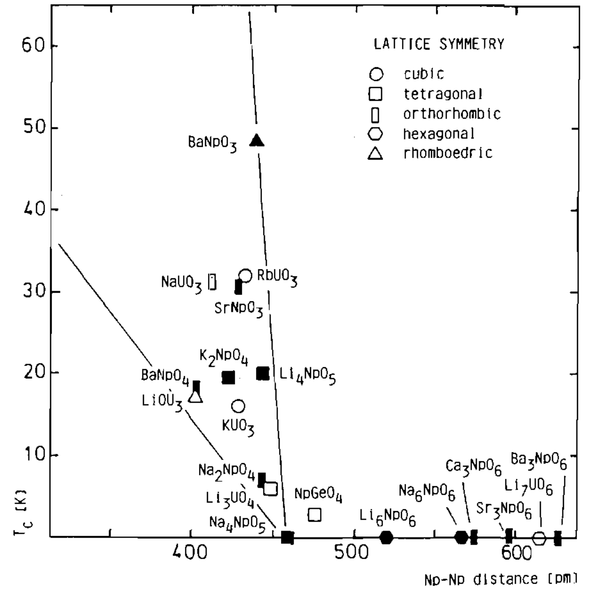

Fig. 4. The transition temperature T_c plotted *vs.* the Np–Np distance shows that for a distance >460 pm no magnetic ordering occurs.

and transition temperatures, respectively, are rather marked and already allow mutual predictions. The trends shown deserve further quantified confirmation.

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